

## PATENT COOPERATION TREATY

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## INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

(Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference CQN2589 WO		<b>FOR FURTHER ACTION</b>		See Form PCT/PEA/416
International application No. PCT/EP2004/012760		International filing date (day/month/year) 11.11.2004	Priority date (day/month/year) 21.11.2003	
International Patent Classification (IPC) or national classification and IPC C08G69/32, C08G69/46, C08G69/04, C08G73/18				
Applicant TEIJIN TWARON B.V. et al.				
<p>1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 5 sheets, including this cover sheet.</p> <p>3. This report is also accompanied by ANNEXES, comprising:</p> <p>a. <input checked="" type="checkbox"/> sent to the applicant and to the International Bureau a total of 4 sheets, as follows:</p> <p><input checked="" type="checkbox"/> sheets of the description, claims and/or drawings which have been amended and are the basis of this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions).</p> <p><input type="checkbox"/> sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. I and the Supplemental Box.</p> <p>b. <input type="checkbox"/> (sent to the International Bureau only) a total of (indicate type and number of electronic carrier(s)) , containing a sequence listing and/or tables related thereto, in computer readable form only, as indicated in the Supplemental Box Relating to Sequence Listing (see Section 802 of the Administrative Instructions).</p>				
<p>4. This report contains indications relating to the following items:</p> <p><input checked="" type="checkbox"/> Box No. I Basis of the opinion</p> <p><input type="checkbox"/> Box No. II Priority</p> <p><input type="checkbox"/> Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability</p> <p><input type="checkbox"/> Box No. IV Lack of unity of invention</p> <p><input checked="" type="checkbox"/> Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement</p> <p><input type="checkbox"/> Box No. VI Certain documents cited</p> <p><input type="checkbox"/> Box No. VII Certain defects in the international application</p> <p><input type="checkbox"/> Box No. VIII Certain observations on the international application</p>				
Date of submission of the demand  15.09.2005		Date of completion of this report  21.10.2005		
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465		Authorized Officer  Gerber, M  Telephone No. +49 89 2399-8528 		

**INTERNATIONAL PRELIMINARY REPORT  
ON PATENTABILITY**

International application No.  
PCT/EP2004/012760

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**Box No. I Basis of the report**

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1. With regard to the **language**, this report is based on the international application in the language in which it was filed, unless otherwise indicated under this item.
- ☐ This report is based on translations from the original language into the following language , which is the language of a translation furnished for the purposes of:
- ☐ international search (under Rules 12.3 and 23.1(b))
  - ☐ publication of the international application (under Rule 12.4)
  - ☐ international preliminary examination (under Rules 55.2 and/or 55.3)
2. With regard to the **elements\*** of the international application, this report is based on *(replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report)*:

**Description, Pages**

1, 4	as originally filed
2, 3, 5	received on 15.09.2005 with letter of 13.09.2005

**Claims, Numbers**

1-4	received on 15.09.2005 with letter of 13.09.2005
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- ☐ a sequence listing and/or any related table(s) - see Supplemental Box Relating to Sequence Listing
3. ☐ The amendments have resulted in the cancellation of:
- ☐ the description, pages
  - ☐ the claims, Nos.
  - ☐ the drawings, sheets/figs
  - ☐ the sequence listing (*specify*):
  - ☐ any table(s) related to sequence listing (*specify*):
4. ☐ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).
- ☐ the description, pages
  - ☐ the claims, Nos.
  - ☐ the drawings, sheets/figs
  - ☐ the sequence listing (*specify*):
  - ☐ any table(s) related to sequence listing (*specify*):

\* If item 4 applies, some or all of these sheets may be marked "superseded."

**INTERNATIONAL PRELIMINARY REPORT  
ON PATENTABILITY**

International application No.  
PCT/EP2004/012760

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**Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

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1. Statement

Novelty (N)	Yes: Claims	1-4
	No: Claims	
Inventive step (IS)	Yes: Claims	1-4
	No: Claims	
Industrial applicability (IA)	Yes: Claims	1-4
	No: Claims	

2. Citations and explanations (Rule 70.7):

**see separate sheet**

**Re Item V**

**Reasoned statement with regard to novelty, inventive step or industrial applicability;  
citations and explanations supporting such statement**

Reference is made to the following documents (D) ; the numbering will be adhered to in the rest of the procedure:

**D1:** US-A-4 172 938

**D2:** US-A-5 646 234

**D3:** US-A-4 018 735

**1. Novelty**

**1.1.** D1, which is considered to represent the closest state of the art, discloses a method for obtaining a composition comprising an aramid by copolymerising a mixture of diamines containing 1,298 g p-phenylene diamine and 0,676 g 5-amino-2-(p-aminophenyl)-benzimidazole, and 3,056 g terephthalic acid dichloride in 30 mL of a mixture of N-methyl-2-pyrrolidone containing 2 wt.% calcium dichloride. The resultant copolymer has a logarithmic viscosity of 5,5 (see example 34). The copolymer is then precipitated, washed with water and dried (see column 7, lines 40-44, and column 14, lines 46-49).

In comparative example V, on page 5 of the application as filed, the Applicant has shown that product according to D1 which has a product value b.c below 50, i.e. outside the claimed range, has the form of a powder and not of crumbs.

Novelty of the subject-matter of **claims 1-4** can therefore be acknowledged over D1.

**1.2.** The same applies to D2.

D2 is also directed to the manufacture of an aramid by polycondensation of 100 mol% terephthaloyl chloride, 40 mol% p-phenylenediamine and 60 mol% 5(6)-amino-2-(p-aminophenyl)-benzimidazole in N-methylpyrrolidone, wherein  $a+b=100$  mol% and the relative viscosity is 4,3 (see example 8).

Solubility-promoting additives such as calcium dichloride in amounts of between 0,2 and

10 wt.%, preferably between 0,5 and 5 wt.%, can be added to the polycondensation mixture (see column 3, lines 19-35 and 62-67).

However, no crumbs are isolated because the aramid is highly soluble in the solvent for the polycondensation and remains completely dissolved therein, the mixture being then used directly for the production of fibres and films (see column 4, lines 40-45).

**1.3.** The novelty of the subject-matter of **claims 1-4** is also acknowledged over D3 because said document is silent as to the obtention of crumbs. Calcium dichloride can be added to the polycondensation mixture (see column 5, lines 28-38) but the aramid is obtained in powdery form instead of crumbs.

## **2. Inventive step**

The objective technical problem to be solved by the present invention is to provide an aramid composition made of terephthaloyl chloride, p-phenylenediamine and 5(6)-amino-2-(p-aminophenyl)-benzimidazole in the form of a crumb or a crumb-like material in order to facilitate its further processing.

The skilled person faced with the above-mentioned problem would not have been prompted by the disclosure of D1, taken alone or in combination with any of D2 or D3, to use calcium dichloride in such an amount that the product b.c is comprised between 50 and 215 (see examples 1-7 and comparative examples I-V).

The subject-matter of **claims 1-4** is therefore to be considered as inventive.

## **3. Industrial applicability**

The subject-matter of present **claims 1-4** appears to comply with the requirements of industrial applicability as stipulated in Article 33(4) PCT.

breakable clumps or particles, which are not sticky and have a mean particle size greater than 100  $\mu\text{m}$ , usually greater than 1 mm. The term crumb in relation to this invention is defined as non-sticky particles, i.e. particles as in powders that do not stick together and remain free to each other, at least 95% of which has an average diameter 0.7-15 mm, preferably 1-7 mm.

Such crumbs are known from the process of preparing of fully aromatic polyamides based on e.g. PPD and TDC, which products are known under the trade names Twaron® (Teijin Twaron) and Kevlar® (DuPont). After polymerization in NMP/ $\text{CaCl}_2$  a crumb is obtained which can be easily coagulated, washed, and dried, and the product obtained can be dissolved in sulfuric acid and shaped into a desired form, like fibers or films.

The monomer of interest, DAPBI (5(6)-amino-2-(p-aminophenyl)-benzimidazole; CAS reg. no: 7621-86-5), is added to the diamine mixture with the objective to obtain a suitable polymer solution right after polymerization with e.g. PPD and TDC, which can be directly shaped into fibers or films, whereby DAPBI is seen as a suitable co-monomer to keep the aramid polymer in solution. It was now found that by selecting a specific ratio of PPD, DAPBI, and  $\text{CaCl}_2$  the formation of powders, paste, dough, and the like could be prevented.

To this end the invention relates to a method for obtaining a composition comprising an aromatic polyamide containing para-phenylene terephthalamide and 2-(p-phenylene)-benzimidazole terephthalamide units by copolymerizing:

- i) a mole % of para-phenylenediamine;
- ii) b mole % of 5(6)-amino-2-(p-aminophenyl)benzimidazole; and
- iii) 90-110 mole% of terephthaloyl dichloride

in a mixture of N-methyl pyrrolidone and containing c wt.% of calcium chloride, wherein c is within the range from 1 to 20, and wherein the ratio a : b ranges from 1 : 20 to 20 : 1, a + b is 100 mole%, and i), ii), and iii) together comprise 1-20 wt.% of the mixture, characterized in that the product b.c is at least 50 and less than 215 and that the composition is a crumb with a relative viscosity  $\eta_{\text{rel}}$  of at least 4, wherein the crumb is defined as non-sticky particles at least 95% of which having an average diameter of 0.7-15 mm.

It is one of the other objectives of the present invention to obtain crumbs comprising a polymer with a sufficient high relative viscosity  $\eta_{\text{rel}}$ . Relative viscosities  $\eta_{\text{rel}}$  of at least 4, more preferably between 4 and 7, most preferably at least 5 can be obtained according

to the method of the invention. It is further preferred to have a mixture for copolymerization wherein b.c is at least 80.

In another object of the invention a method for obtaining a purified aromatic polyamide is obtained by coagulating and washing the obtained crumb with water, followed by drying. The drying step can be performed according to standard procedures, such as ambient conditions, or at elevated temperature and/or lowered pressure. The thus obtained material is suitable for making a spin dope by dissolving it in a solvent, for instance sulfuric acid, NMP, NMP/CaCl<sub>2</sub>, dimethylacetamide, and the like. The dope can be used to manufacture formed articles, such as fibers, films, and the like.

In the following experiments, the aspects of the invention are exemplified.

#### General polymerization procedure

DAPBI (ex Spektr T.T.T., Russia) was dried under vacuum for 1 h at 160° C. PPD (Teijin Twaron), TDC (freshly distilled), NMP/CaCl<sub>2</sub> and NMP (both ex Teijin Twaron) were used as received (moisture content 80 ppm).

The glassware was pre-dried for 1 h in an air circulation oven at 120° C. A clean and dry 2 l flask was supplied with a mechanical stirrer, N<sub>2</sub>-inlet and outlet, and vacuum supply. Generally, the N<sub>2</sub>-stream is between 40 – 60 ml/min. A large part (400 ml) of the solvent and the precisely pre-weighed amines were carefully brought in the reactor. The reactor was closed and purged two times with nitrogen. The mixture was stirred for 30 min at 150 rpm and heated to 60° C and mixed for 0.5 h to dissolve or disperse the amines properly. The flask was cooled with ice/water to 5 – 10° C. After removing the coolant, the stirrer velocity was set at 320 rpm and a precisely pre-weighed amount of the acid chloride was brought into the vessel through a funnel. In all cases the mol ratio of the total number of amines and the acid chloride equals one. The flask, which contained the acid chloride and the funnel, were rinsed with the remaining solvent (50 ml). The vessel was closed and the mixture was allowed to react for at least 30 min (nitrogen flush between 40 – 60 ml/min). The stirring was stopped and the reaction vessel was removed.

The crumbed product together with demi-water was gently added into a Condux LV15 15/N3 coagulator and the mixture was collected on an RVS filter. The product was washed 4 times with 5 l of demi-water, collected in a 2 l glass beaker and dried under vacuum for 24 h at 80° C.

Table

Examples	PPD a mole%	DAPBI b mole %	CaCl <sub>2</sub> c wt. %	b.c	$\eta_{rel}$	$\eta_{inh}$	crumb
1	90	10	10.40	104.0	6.29	6.46	yes
2	90	10	11.55	115.5	5.93	6.2 <sup>#</sup>	yes
3	80	20	9.85	197.0	5.38	5.92	yes
4	80	20	10.28	205.6	4.10	5	yes
5	60	40	4.77	190.8	5.69	6.01	yes
6	33	67	3.09	207.0	6.98	6.45	yes
7	30	70	2.82	197.4	6.2 <sup>*</sup>	6.3 <sup>#</sup>	yes
Comparative Examples							
I	80	20	11.55	231.0	4.59	5.3 <sup>#</sup>	dough/paste
II	60	40	5.49	219.6	5.87	6.2	dough/paste
III	33	67	4.56	306.9	2.75	3.58	dough/paste
IV	33	67	2.88	193.0	2.31	3.04	gel <sup>*</sup>
V	80	20	1.96	39.2	1.56	1.93	powder

average of 3 values

<sup>#</sup> calculated value<sup>\*</sup> gel with precipitated particles

The Table shows the advantageous properties when the conditions of the invention are satisfied. For instance Comparative example V (according to US 4,172,938) has a product b.c value outside the claimed range (39.2) and a relative viscosity below 4 (1.56). No crumb is formed, but a powder (having a particle size far below the average diameter 0.7 mm).



## Claims:

1. A method for obtaining a composition comprising an aromatic polyamide containing para-phenylene terephthalamide and 2-(p-phenylene)benzimidazole terephthalamide units by copolymerizing:
- 5 i) a mole % of para-phenylenediamine;  
ii) b mole % of 5(6)-amino-2-(p-aminophenyl)benzimidazole; and  
iii) 90-110 mole% of terephthaloyl dichloride  
in a mixture of N-methyl pyrrolidone and containing c wt.% of calcium chloride, wherein c is within the range from 1 to 20, and wherein the ratio a : b ranges from 1 : 20 to 20 : 1, a + b is 100 mole%, and i), ii), and iii) together comprise 1-20 wt.% of the mixture,
- 10 characterized in that the product b.c is at least 50 and less than 215 and that the composition is a crumb with a relative viscosity  $\eta_{rel}$  of at least 4, wherein the crumb is defined as non-sticky particles at least 95% of which having an average diameter of 0.7-15 mm.
- 15 2. A composition comprising an aromatic polyamide containing para-phenylene terephthalamide and 2-(p-phenylene)benzimidazole terephthalamide units, obtainable by copolymerizing para-phenylenediamine; 5(6)-amino-2-(p-aminophenyl)benzimidazole; and terephthaloyl dichloride in a mixture of N-methyl pyrrolidone and calcium chloride,
- 20 characterized in that the composition is a crumb with a relative viscosity  $\eta_{rel}$  of at least 4.
3. The composition of claim 2 wherein the crumb has a relative viscosity  $\eta_{rel}$  between 4 and 7:
- 25 4. A method for making purified aromatic polyamide by coagulating and washing the crumb of claim 2 or 3 in water, followed by a drying step.